

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09D 1/00, 5/00, C09K 3/18	A1	(11) International Publication Number: WO 97/23571 (43) International Publication Date: 3 July 1997 (03.07.97)
(21) International Application Number: PCT/US96/18986 (22) International Filing Date: 27 November 1996 (27.11.96) (30) Priority Data: 08/576,255 21 December 1995 (21.12.95) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: SCHOLZ, Matthew, T.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). KAUSCH, William, L.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: SPRAGUE, Robert, W. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COATING COMPOSITION HAVING ANTI-REFLECTIVE AND ANTI-FOGGING PROPERTIES (57) Abstract A coating composition which imparts anti-reflective and anti-fog properties to substrates coated therewith. The coating composition utilizes an inorganic metal oxide in combination with particular polyhydroxy surfactants. The coating compositions are particularly useful in the manufacture of disposable surgical masks and face shields.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**COATING COMPOSITION HAVING ANTI-REFLECTIVE
AND ANTI-FOGGING PROPERTIES**

5 **Technical Field**

 This invention relates generally to coating compositions and methods for producing optically clear articles with very low reflection and exceptional anti-fogging properties even under high humidity conditions. Such properties are desirable in articles such as face shields used for personal protection, ophthalmic
10 lenses, architectural glazings, windows, automotive windshields and the like.

BACKGROUND ART

 There are numerous instances where optically clear articles would be enhanced if the tendency of the articles to cause glare or to be obscured by the formation of a fog on a surface of the article could be reduced. For example,
15 protective eyewear (goggles, face shields, helmets, etc.), ophthalmic lenses, architectural glazings, decorative glass frames, motor vehicle windows and windshields may all reflect light in a manner that causes an annoying and disruptive glare. Use of such articles may also be detrimentally affected by the formation of a moisture vapor fog on a surface of the article.

20 Glare is the undesirable reflection of light from a surface upon which the light is incident. In general, glare may be reduced by increasing the amount of light transmitted by the article, thereby reducing the amount of light which is available for reflection. Alternatively, the article surface can be modified (e.g., roughened, embossed, etc.) to cause the light to be reflected from the article more randomly
25 and, therefore, with less glare.

 Coatings which significantly increase the percent transmission of light and provide articles having very low reflection ("anti-reflective coatings") are known in the art. For example, U.S. Patent No. 4,816,333 to Lange et al. (also assigned to 3M) discloses anti-reflective coatings of silica particles. The coating solution
30 contains colloidal silica particles and optionally a surfactant ("Triton™ X-100" and "Tergitol™ TMN-6") to improve the wettability of the coating solution. U.S.

Patent No. 4,374,158 (Taniguchi et al.) discloses an anti-reflective coating using a gas phase treatment technique. The coating may optionally contain additives as surface controlling agents, such as silicone type surfactants. Various other types of anti-reflective coatings are disclosed in U.S. Patent Nos. 2,366,516; 3,301,701; 3,833,368; 4,190,321, 4,271,210; 4,273,826; 4,346,131 and 4,409,285; by Cathro et al. in "Silica Low-Reflection Coatings for Collector Covers by a Dye-Coating Process," Solar Energy, Vol. 32, No. 5, pp. 573-579 (1984); and by J.D. Masso in "Evaluation of Scratch Resistant and Anti-reflective Coatings for Plastic Lenses," Proceedings of the 32nd Annual Technical Conference of the Society of Vacuum Coaters, Vol. 32, p. 237-240 (1989). None of these anti-reflective coatings produce a durable anti-fog coating.

In general, fog formation occurs under conditions of high humidity and high temperature or at interfacial boundaries where there is a large temperature and humidity difference. Coatings which reportedly reduce the tendency for surfaces to "fog up" (i.e., anti-fogging coatings) are known. For example, U.S. Patent No. 3,212,909 to Leigh discloses the use of ammonium soap, such as alkyl ammonium carboxylates in admixture with a surface active agent which is a sulfated or sulfonated fatty material, to produce an anti-fogging composition. U.S. Patent No. 3,075,228 to Elias discloses the use of salts of sulfated alkyl aryloxypolyalkoxy alcohol, as well as alkylbenzene sulfonates, to produce an anti-fogging article useful in cleaning, and imparting anti-fog properties to various surfaces. U.S. Patent No. 3,819,522 to Zmoda, discloses the use of surfactant combinations comprising derivatives of decyne diol as well as surfactant mixtures which include ethoxylated alkyl sulfates in an anti-fogging window cleaner surfactant mixture.

Japanese Patent Kokai No. Hei 6[1994]-41335 discloses a clouding and drip preventive composition comprising colloidal alumina, colloidal silica and an anionic surfactant.

U.S. Patent No. 4,478,909 (Taniguchi et al.) discloses a cured anti-fogging coating film which comprises polyvinyl alcohol, a finely divided silica, and an organic silicon compound, the carbon/silicon weight ratio apparently being important to the film's reported anti-fogging properties. Various surfactants,

including fluorine-containing surfactants, may be used to improve the surface smoothness of the coating.

Other anti-fog coatings incorporating surfactants are described in U.S. Patents 2,803,552; 3,022,178 and 3,897,356. "Anti-fog Antistat Eases Processing Problems," Modern Plastics, Oct. 1988, discusses antistat agents, including alkyl sulfonates, and anti-fog agents for use in plastic films. Furthermore, American Cyanamid Industrial Chemical Division markets "Aerosol OT Surface Active Agent" (dioctylsodium-sulfosuccinate), which is advertised as useful to prepare an anti-fog composition for direct application to glass.

None of the above-described coatings which reduce the tendency for an article to fog have anti-reflective properties. Furthermore, in general, the anti-fog compositions of the prior art rely on high solution concentrations (e.g., in excess of 0.2 percent, and typically in concentrations in excess of 5 percent by weight) of surfactant and other organic additives to provide an anti-fog effect. When used at such high concentrations, the surfactants and other organic additives would interfere with and significantly reduce the anti-reflective properties provided by porous coatings, such as metal oxides.

Face masks and shields which are described as having anti-fog and anti-glare properties are known. For example, the "SHIELDMATE" by IREMA U.S.A. Ltd. of Chicopee, M.A. is described in U.S. Patent No. 4,944,294 (Borek). The hospital face mask is described as including a transparent plastic eye shield coated with any suitable anti-fogging, anti-glare silicone agent, such as a dimethylsiloxane polymer.

World Patent Application No. 89/10106 (Russell) discloses a surgical mask/face shield combination. The face shield is coated with an anti-fog coating, such as that described in U.S. Patent No. 4,467,073. These coatings are made by combining, for example, polyvinylpyrrolidone, a surfactant, and a curable isocyanate functional prepolymer. Additionally, Infection Control Products, Inc., markets the "AGAFAR Adjustable Flip-Up Face Shield" which is advertised as being anti-glare, anti-fog and anti-reflective. However, none of these products utilize a porous coating and none display an increase in transmission of visible light through the coated article of more than 2 to 3 percent greater than the uncoated article. It is

understood that an increase in percent transmission corresponds to a decrease in percent reflection, provided the sample is transparent (i.e., non-light-absorbing and not hazy). Accordingly, a need exists for a coating composition which will impart anti-fog properties to a substrate coated therewith, while increasing the percent transmission, and correspondingly decreasing the percent reflection, of incident light through the substrate, such that the substrate is truly "anti-reflective."

SUMMARY OF THE INVENTION

The present invention provides coating compositions which impart both anti-reflection and anti-fog properties to substrates coated therewith. By "anti-reflective" it is meant that the percent transmission of a light transmissive substrate coated with the coating composition is increased by at least 3 percent over the uncoated substrate measured using 550 nm light. The coating composition utilizes an inorganic metal oxide in combination with particular nonionic surfactants which are present in a concentration which imparts a durable anti-fog property to the coated substrate, yet does not destroy the anti-reflective properties provided by the metal oxide.

The present invention provides a coating composition comprising:

- (a) inorganic metal oxide particles;
- (b) a surfactant comprised of at least one hydrophobic group and at least one hydrophilic group, wherein

(1) the hydrophilic group is selected from the group consisting of

- (i) pyrrolidone, and
- (ii) a polyhydroxyl group comprising at least two hydroxyl groups, wherein at least two of the hydroxyl groups are separated by no more than 5 atoms, and the number of said hydroxyl groups is greater than or equal to the total number of hydrophobic groups present within the surfactant molecule, and

(2) wherein the hydrophobic group is a hydrocarbon chain comprising at least 4 carbon atoms or a perfluorinated radical comprising at least 3 carbon atoms, and wherein the coating composition when coated on at least one side of a light transmissive substrate:

1) exhibits a drop diameter of at least 4 mm when tested in accordance with the Wetting Test described herein; and

2) provides said substrate with a percent transmission at 550 nm which is at least 3 percent greater than that of the uncoated substrate.

The compositions may optionally contain a coupling agent (e.g. a silane) and/or a polymeric binder that improves adhesion of the dried coating to the substrate.

Preferred coating compositions applied to at least one side of a light transmissive substrate increase the percent transmission of the substrate by at least 3 percent, and preferably by about 5 to 10 percent, while resisting fogging even upon exposure to "steam," i.e., warm air saturated with water. The anti-fog property is shelf stable and deteriorates very slowly when exposed to accelerated aging conditions, as described hereinafter. Ideally, in preferred embodiments, the coated articles have exceptional anti-fog properties while also having greater than 96 percent transmission of 550nm light.

The compositions may be applied to a wide variety of substrates by a variety of coating methods. Accordingly, the invention provides protective eyewear, such as surgical masks and face shields, as well as ophthalmic lenses, windows and windshields which have anti-reflective and anti-fog properties.

The invention also relates to a method of imparting anti-reflection and anti-fogging properties to a substrate. The method comprises the steps of providing a substrate, preparing a coating composition having the formulation described above, applying the coating composition to the substrate, and drying the coating composition.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Anti-reflection

The anti-reflective properties of the coatings of this invention are provided by a porous inorganic metal oxide network. More particularly, the coating
5 compositions of the invention when coated on a substrate and dried provide a continuous and highly porous network of metal oxide particles. As used herein, the term "continuous" refers to a coating having no visible discontinuities or gaps. The term "network" (as used herein) refers to a porous, three-dimensional structure, preferably formed by an aggregation of colloidal particles linked together. The
10 network is held together through particle/particle, particle/coupling agent or particle/coupling agent/particle bonds, providing a coating having integrity which does not flake off by simple flexing and/or use of the coated article.

The term "porous" refers to the presence of voids between the inorganic metal oxide particles created when the particles pack together. For single layer
15 coatings, it is known that in order to maximize light transmission in air through an optically transparent substrate, and minimize reflection by the substrate, the refractive index of the coating should equal as closely as possible the square root of the refractive index of the substrate and the thickness of the coating should be one-fourth ($\frac{1}{4}$) of the optical wavelength of the incident light. The voids in the coating
20 provide a multiplicity of subwavelength interstices between the metal oxide particles where the index of refraction (IR) abruptly changes from that of air (IR=1) to that of the metal oxide particles (e.g., for silica IR=1.44). By adjusting the porosity, a coating having a calculated index of refraction (as shown in U.S. Patent No. 4,816,333 (Lange, et al.) incorporated herein by reference) very close to the square
25 root of the refractive index of the substrate can be created. By utilizing coatings having optimal indices of refraction, at coating thicknesses equal to approximately one-fourth the optical wavelength of the incident light, the percent transmission of light through the coated substrate is maximized and reflection is minimized.

The voids in the coating are present substantially throughout; however, the
30 coating may vary in density, e.g., the coating may become gradually more porous moving away from the substrate producing a gradient density. Such a gradient

density enhances the anti-reflective property of the coating. Preferably, the network has a porosity of about 25 to 45 volume percent, more preferably about 30 to 40 volume percent, when dried. Porosity may be calculated from the refractive index of the coating according to published procedures such as in W. L. Bragg, A. B. Pippard, Acta Crystallographica, volume 6, page 865 (1953). When the metal oxide is silicon dioxide, this porosity provides a coating having an index of refraction of 1.2 to 1.4, preferably 1.25 to 1.36, which is approximately equal to the square root of the refractive indices of polyester, polycarbonate, or polymethyl methacrylate substrates. For example, a porous silica coating having a refractive index of 1.25 to 1.36 is capable of providing a highly anti-reflective surface when coated on a polyethylene terephthalate substrate ($n=1.64$) at a thickness of 1000-1200Å.

The metal oxide component of the present invention is preferably silica (essentially silicon dioxide with or without other additives or impurities) but may alternatively be aluminum oxide, tin oxide, titanium oxide, antimony oxide, zirconium oxide, as well as mixtures and combinations thereof. The metal oxide particles should be less than about 200nm in diameter in order to provide effective anti-reflective properties. Preferably the average particle diameter is less than 70nm, more preferably less than 20nm, and most preferably between about 4 and 8nm. Although the particles are preferably spherical, other shapes are possible including irregular and fibrous shapes. The metal oxide concentration is preferably from about 0.1 to 15 percent by weight of the coating solution, more preferably from about 0.5 to 5 percent by weight. Above about 15 percent by weight the coating solution becomes difficult to apply in the desired thickness range and below about 0.1 percent by weight, excessive time periods are required for the coating to dry after application to the substrate. The term "solution" as used herein includes dispersions or suspensions of finely divided inorganic metal oxide particles in a liquid medium.

The metal oxide is most conveniently coated on the substrate as a colloidal dispersion (referred to herein as a "sol") which comprises finely divided solid inorganic metal oxide particles in an aqueous or an organic liquid. The sol may be

acid or base stabilized. Preferably the sol is base stabilized, for example, using sodium hydroxide, ammonium hydroxide, potassium hydroxide and the like.

Sodium hydroxide base stabilized sols having a pH of 9 to 11 are most preferred and include "NALCO 1115" and "NALCO 1130," commercially available from
5 NALCO Chemical Co., "Remasol SP30," commercially available from Remet Corp., and "LUDOX SM," commercially available from E. I. Du Pont de Nemours Co., Inc.

Anti-fog

The coating compositions of the present invention provide anti-fog
10 properties, in addition to anti-reflection, to substrates coated therewith. Coatings are considered anti-fogging if a coated substrate resists the formation of small, condensed water droplets in sufficient density to significantly reduce the transparency of the coated substrate such that it cannot be adequately seen through, after exposure to repeated human breathing directly on the article and/or after
15 holding the article above a "steam" jet. A coating composition may still be regarded as anti-fogging even though a uniform water film or a small number of large water droplets forms on the coated substrate so long as the transparency of the coated substrate is not significantly reduced such that it cannot be readily seen through. In many instances, a film of water that does not significantly reduce the transparency
20 of the substrate will remain after the substrate has been exposed to a "steam" jet.

The compositions of the present invention derive their anti-fogging property by incorporation of a particular surfactant or combination of surfactants which render surfaces to which the compositions are applied hydrophilic. The term
"surfactant" as used herein describes molecules comprising hydrophilic (polar) and
25 hydrophobic (non-polar) regions on the same molecule which are sizable enough to be capable of reducing the surface tension of the coating solution and providing a coating which imparts anti-fog properties to substrates or articles coated therewith. Certain surfactants of the present invention comprise multiple hydrophilic and or hydrophobic regions on the same molecule.

30 Useful surfactants of the present invention comprise at least one hydrophilic group which is a pyrrolidone group, or a polyhydroxyl group having at least two

hydroxyl groups wherein at least two of the hydroxyl groups are separated by no more than 5 atoms and the total number of hydroxyl groups is equal to, or preferably greater than, the total number of hydrophobic groups present within the surfactant molecule.

5 The requirement that the surfactant include a hydrophilic group which is either a pyrrolidone group or a polyhydroxyl group, or both, is an important one. Applicants have found that surfactants such as the nonionic surfactants based on repeating units of ethylene oxide and propylene oxide (e.g., "Pluronic Block Copolymer Surfactants" and "Tetronic™ Block Copolymer Surfactants," both
10 commercially available from BASF Corp., Performance Chemicals, Parsippany, New Jersey), as well as those based on tetramethyldodecane diol (e.g., "Surfynol 104," commercially available from Air Products and Chemicals, Inc., Allentown, Pennsylvania), do not produce a durable anti-fog coating when used with porous metal oxide networks. Additionally, polyethoxylated alcohols, such as "Tergitol™
15 TMN-6," commercially available from Union Carbide Chemical and Plastics Co., Industrial Chemicals Division, Danbury, Connecticut, polyethoxylated alkyl phenols, such as "TRITON™ X-100," also commercially available from Union Carbide, and amine oxides, such as "Rhodamox LO," commercially available from Rhone-Poulenc, Surfactant and Specialty Division, Dalton, Georgia, do not produce
20 durable anti-fog coatings when used with porous metal oxide networks. Cationic surfactants such as 3-lauramidopropyltrimethyl-ammonium methosulfate (commercially available as "Cyastat™ LS Antistatic Agent", from Cytec Industries, Stamford, Conn.) and myristyl trimethylammonium bromide also do not produce durable anti-fog coatings when used with porous metal oxide networks.

25 Useful surfactants comprise at least one hydrophobic group which comprises a hydrocarbon chain comprising at least four carbon atoms, and/or a perfluorinated group comprising at least three carbon atoms. Surfactants containing a perfluorinated group preferably include a perfluorinated radical group of at least six carbons, more preferably at least eight carbon atoms. Surfactants which do not
30 include a perfluorinated group preferably have a hydrocarbon chain of at least eight, and more preferably, at least twelve carbon atoms.

The surfactants of the present invention in order to be immobilized on the substrate at room temperature, preferably also possess at least one of the following characteristics.

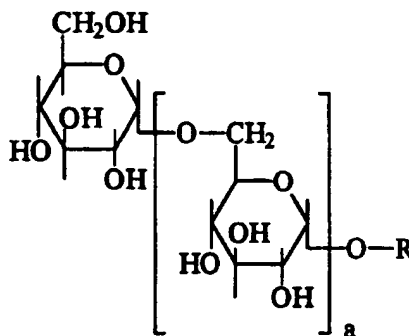
1. The surfactant has a melting point greater than room temperature, i.e., greater than about 20°C, preferably greater than about 30°C, and most preferably greater than 40°C.
2. The surfactant is relatively insoluble in water. Preferably the surfactant has a solubility in water of less than about 10 percent by weight, more preferably less than about 1 percent by weight and most preferably less than about 0.1 percent by weight, at 23°C. Relatively insoluble surfactants are preferred since they are less likely to rehydrate, dissolve, and reorient, even under high humidity conditions.
3. The surfactant is capable of being covalently bound to metal oxide. The surfactant may itself react with the metal oxide, or may be chemically bound to the metal oxide through the use of a coupling agent, as described in further detail hereinbelow.

Surfactant Chemistry

The following surfactant classes and surfactants have been found to be particularly useful, individually or in combination, in the practice of the present invention:

1. Alkyl or Aralkylpolyglucosides

Surfactants within this class have the general formula:



wherein

R is an alkyl group having about 4 to 36, preferably about 12 to 22, carbon atoms, an aralkyl group having about 7 to 36 carbon atoms, or a perfluorinated alkyl group having about 3 to 12 carbon atoms, and

a = about 0-20, preferably about 1-10.

5 Examples of preferred surfactants within this class are alkyl polyglucosides. Examples of commercially available surfactants of this class include “Glucopon™ 625CS” and “Glucopon™ 225” available from the Henkel Corp. Emery Group Ambler, PA.

2. Alkyl or Aalkyl Glyceryl Esters

10 Surfactants within this class have the general formula:

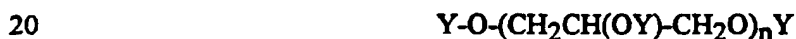


wherein R is as described hereinabove.

Examples of preferred surfactants within this class are glycerol monostearate and glycerol monolaurate. Examples of commercially available surfactants of this class include "Luaricidin™" (glycerol monolaurate) and "Cerasynt GMS" (glycerol monostearate), available from Luaricidin, Inc., East Lansing, MI, and ISP Van Dyk Inc., Belleville, NJ, respectively.

3. Alkyl or Aralkyl Polyglycerol Esters

Surfactants within this class have the general formula:



wherein Y is OH or -C(O)R, where R is an alkyl group having about 8 to 36 carbon atoms, or an aralkyl group having about 7 to 36 carbon atoms, or a perfluorinated alkyl group of about 3 to 12 carbon atoms, provided that at least two Y groups are hydroxyl groups and the number of hydroxyl groups is equal to or greater than the number of hydrophobic groups, and

n = about 2-20, preferably about 4-10.

Examples of preferred surfactants within this class are alkyl polyglycerol esters. Examples of commercially available surfactants of this class include "Caprol 6G2S" and "Caprol 6G2O," available from Karlshamns, Columbus, OH. Also preferred are alkylphenoxypolyglycerol esters such as "Surfactant 10G" available from Olin Corp., Stamford, CT.

4. Alkyl or Aralkyl Diethanolamides

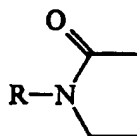
Surfactants within this class have the general formula:



wherein R is as described herein above. Examples of preferred surfactants within this class are alkyl diethanolamides. Examples of commercially available surfactants of this class include "Chemstat LD-100" (lauric diethanolamide) available from Chemax, Greenville, SC, and "Lipamide S" (stearyl diethanolamide) available from Lipo Chemical, Paterson, NJ.

5. Alkyl or Aralkyl Pyrrolidones

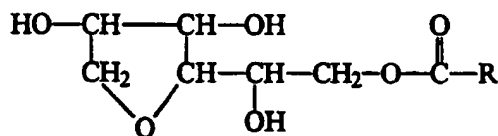
Surfactants within this class have the general formula:



wherein R is as described hereinabove. Examples of preferred surfactants within this class are alkyl pyrrolidones. Examples of commercially available surfactants of this class include "Surfadone™ LP-100" and "Surfadone™ LP-300" Specialty Surfactants available from ISP Technologies, Wayne, NJ.

6. Alkyl or Aralkyl Sorbitan Esters

Surfactants within this class have the general formula:



where R is described hereinabove. Examples of preferred surfactants within this class include Span 80 and sorbitan monostearate, available from ICI Americas Inc., Wilmington, DE.

Applicants have discovered that the above-described surfactants of the present invention can be utilized in concentrations which are effective to provide the coating composition with anti-fog properties, yet will not destroy the anti-reflective effects produced by the inorganic metal oxide. The anti-reflective property of the coating may be decreased by the surfactant, or by other additives, by one or both of

two means. First, if too much surfactant is added, the void volume of the coating decreases thereby increasing the refractive index of the coating beyond that desired for maximum transmission of light. Secondly, the refractive index of the surfactant or additive can itself influence the refractive index of the coating. In general, the highest concentration of surfactant which will not adversely effect the anti-reflective property of the coating composition or the coating quality is preferred. Surfactants of lower refractive indices may be tolerated at higher concentrations on a weight basis. Rinsing or steeping the coated article in water may be desirable to remove excess surfactant or other additive. For typical concentrations of metal oxide (e.g., about 1 to 5 percent by weight) most surfactants comprise less than about 0.15 percent by weight of the coating composition, preferably less than 0.10 percent by weight, more preferably between about 0.003 and 0.05 percent by weight, and most preferably between about 0.01 and 0.05 percent by weight, in order to preserve the anti-reflective properties of the coating. On a solids basis the surfactant should be present at less than 10 percent by weight of the metal oxide, preferably less than 5 percent, more preferably less than 2.5 percent, and most preferably between 0.25 and 2.5 percent by weight of the metal oxide. It should be noted that with some surfactants a spotty coating is attained at concentrations in excess of what is needed to achieve the anti-fog property.

The surfactant may be applied as part of the metal oxide coating composition or may be applied, preferably in an aqueous or hydroalcoholic medium, as an "overcoat", i.e., can be applied as a separate coating solution over a previously deposited metal oxide coating. Preferably, the surfactant is added directly to the metal oxide sol coating composition to simplify the coating process and to minimize any risk of scratching the metal oxide layer.

Other Additives

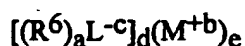
The surfactants of the present invention may be utilized alone or in combination with the anionic surfactants described in commonly assigned United States Patent Application No. 08/354,242, filed December 12, 1994, incorporated herein by reference.

A particularly useful anionic surfactant comprises at least one hydrophilic anionic group. The anionic group may be $-\text{OSO}_2\text{O}^-$, $-\text{SO}_2\text{O}^-$, $-\text{CO}_2^-$, $(-\text{O})_2\text{P}(\text{O})\text{O}^-$, $\text{OP}(\text{O})(\text{O}^-)_2$, $-\text{P}(\text{O})(\text{O}^-)_2$, $-\text{P}(\text{O}^-)_2$, $-\text{OP}(\text{O}^-)_2$, $(-\text{SO}_2)_2\text{N}^-$, $-\text{SO}_2\text{N}(\text{R}'')^-$, $(-\text{SO}_2)_2\text{C}-\text{H}$ or $-\text{N}^+(\text{R}'')_2(\text{CH}_2)_x\text{L}'$, wherein R'' is hydrogen, an alkyl group which is unsubstituted or substituted with atoms independently selected from the group consisting of oxygen, nitrogen and sulfur, or an alkylene carboxyl group, which alkyl or alkylene group comprises about 1 to 10 carbon atoms; and x is 1 to 4; and L' is selected from the group consisting of $-\text{OSO}_2\text{O}^-$, $-\text{SO}_2\text{O}^-$, $(-\text{O})_2\text{P}(\text{O})\text{O}^-$, $-\text{OP}(\text{O})(\text{O}^-)_2$, $-\text{P}(\text{O})(\text{O}^-)_2$, and $-\text{CO}_2^-$. Each anionic group is associated with at least one cation such that the ratio of total anionic charge of the surfactant molecule to the total cationic charge of the surfactant molecule equals 1, making the net charge of the surfactant molecule neutral. The cation(s) are selected from the group consisting of hydrogen, sodium, potassium, lithium, ammonium, calcium, magnesium, aluminum, strontium, and $\text{R}'''\text{A}$ groups, wherein R''' is R^4 or R^5 , and wherein R^4 is hydrogen or an alkyl or cycloalkyl group of about 1 to 10 carbon atoms, and R^5 is covalently bonded to the surfactant molecule and is an alkyl bridging group of 1 to 10 carbon atoms, and A is selected from N^+R^4_3 ; a guanidinium ion optionally substituted with oxygen, nitrogen or sulfur atoms; or N^+B wherein B comprises 3 to 7 atoms selected from the group consisting of carbon, nitrogen, sulfur and oxygen atoms which complete the nitrogen containing heterocyclic ring; and wherein any R^4 or R^5 group may be unsubstituted or substituted with oxygen, nitrogen or sulfur atoms. Of course, cations having a charge greater than one may be associated with more than one anion, e.g., $(\text{SO}_4)_2\text{Ca}$ or $(\text{SO}_3)_2\text{Mg}$. The anionic group may be the sole hydrophilic group or may be covalently bound to other hydrophilic groups such as ester, thio- ester, ether, amide, urea, urethane, hydroxyl, and amine groups and polymers comprising these groups and having molecular weights less than about 5,000, and preferably less than about 2,000 (e.g., an anionic derivative of a polyethoxylated surfactant).

Useful anionic surfactants having a carboxylate group as the hydrophilic group further comprise an additional polar substituent capable of stabilizing the ionic form of the surfactant. Preferably, the additional polar substituent is no further than four atoms removed from the carbon of the carboxylate group. The added polar substituent is preferably an ether, amide, alcohol, carboxyl, ester, urea or urethane group.

Useful anionic surfactants of the type described above comprise at least one hydrophobic group which is a hydrocarbon chain comprising at least four carbon atoms, or a perfluorinated group comprising at least three carbon atoms. Surfactants containing a perfluorinated group preferably include a perfluorinated radical group of at least six carbons, more preferably at least eight carbon atoms. Surfactants which do not include a perfluorinated group preferably have a hydrocarbon chain of at least eight, and more preferably, at least twelve carbon atoms.

Particularly useful anionic surfactant additives have the following general structure:



wherein:

R^G is a perfluorinated alkyl or cycloalkyl group of about 3 to 18 carbon atoms; a polyethoxylated perfluoroalkyl or perfluorocycloalkyl substituted alcohol comprising about 3 to 18 perfluorinated carbon atoms and about 0 to 30 non-fluorinated carbon atoms; a perfluoroalkyl substituted alkyl or alkenyl group of about 3 to 18 perfluorinated atoms and about 0 to 30 non-fluorinated carbon atoms, which alkyl or alkenyl group optionally comprises oxygen, nitrogen or sulfur atoms within or substituted upon the alkyl or alkenyl chain; an alkyl or alkenyl group (straight or branched chain) of about 4 to 36 carbon atoms, which alkyl or alkenyl group optionally comprises oxygen, nitrogen or sulfur atoms within or substituted upon the alkyl or alkenyl chain; an aralkyl group of about 7 to 36 carbon atoms, which aralkyl group is optionally independently substituted in available positions by oxygen, nitrogen or sulfur atoms; or a polyethoxylated or polypropoxylated alkyl or aralkyl group which alkyl or aralkyl group comprises about 7 to 36 carbon atoms;

L is a sulfate ($-\text{OSO}_2\text{O}^-$), sulfonate ($-\text{SO}_2\text{O}^-$), phosphate ($(-\text{O})_2\text{P}(\text{O})\text{O}^-$ or $-\text{OP}(\text{O})(\text{O}^-)_2$), phosphonate ($-\text{P}(\text{O})(\text{O}^-)_2$), sulfonimide ($(-\text{SO}_2)_2\text{N}^-$), sulfonamide ($-\text{SO}_2\text{N}(\text{R}')^-$), carboxylate ($-\text{CO}_2^-$), phosphonite ($-\text{P}(\text{O}^-)_2$), phosphite ($-\text{OP}(\text{O}^-)_2$), or disulfonylmethide ($(-\text{SO}_2)_2\text{C-H}$). Amphoteric alkyl forms of the above groups

5 are also useful, including groups having the formula $-\text{N}^+(\text{R}^7)_2(\text{CH}_2)_x\text{L}'$, wherein R^7 is hydrogen or an alkyl or alkylene group optionally substituted with nitrogen, oxygen or sulfur atoms; or an alkylene carboxyl group, which alkyl or alkylene carboxyl group comprises about 1 to 10 carbon atoms; $x = 1$ to 4; and L' is $-\text{OSO}_2\text{O}^-$, $-\text{SO}_2\text{O}^-$, $(-\text{O})_2\text{P}(\text{O})\text{O}^-$, $-\text{OP}(\text{O})(\text{O}^-)_2$, $-\text{P}(\text{O})(\text{O}^-)_2$, $-\text{CO}_2^-$, $-\text{P}(\text{O}^-)_2$, or $-\text{OP}(\text{O}^-)_2$; provided that when L is a carboxylate, R^6 further comprises an additional

10 polar heteroatom or substituent no further than four, and preferably no further than three, atoms removed from the carboxylate group wherein said polar substituent is an ether, amide, alcohol, carboxyl, ester, thioester, urea, or urethane group, or combinations thereof including oligomers comprising these polar groups;

15 M is hydrogen (H^+), sodium (Na^+), potassium (K^+), lithium (Li^+), ammonium (NH_4^+), calcium (Ca^{+2}), magnesium (Mg^{+2}), strontium (Sr^{+2}), aluminum (Al^{+3}) or R^mA^+ , wherein R^m is R^4 or R^5 , wherein R^4 is hydrogen or an alkyl or cycloalkyl group of about 1 to 10 carbon atoms and R^5 is covalently bonded to the surfactant molecule and is an alkyl bridging group of about 1 to 10

20 carbon atoms, and A^+ is selected from the group consisting of N^+R^4_3 , (e.g., $\text{N}^+(\text{CH}_3\text{R}^4)_4$, $\text{HN}^+(\text{CH}_2\text{CH}_2\text{OH})_3$, $\text{H}_2\text{N}^+(\text{CH}_2\text{CH}_2\text{OH})_2$); a guanidinium ion optionally substituted with oxygen, nitrogen or sulfur atoms; or a heterocyclic N^+B wherein B comprises 3 to 7 atoms selected from the group consisting of carbon, nitrogen, sulfur and oxygen atoms which complete the nitrogen containing

25 heterocyclic ring; and wherein R^5 and R^4 may be substituted in available positions with oxygen, nitrogen or sulfur atoms;

a and c are independently 1 or 2;

b and d are independently 1, 2 or 3; and

e is equal to (c times d)/b, or zero in the case of amphoteric surfactants.

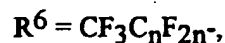
When R⁴ is a polyethoxylated or polypropoxylated substituent or a copolymer of ethylene oxide and propylene oxide, these polymeric subunits are present in amounts of 1 to 100 moles, preferably about 1 to 20 moles per mole of surfactant.

5 The following surfactant classes and surfactants are particularly useful individually or in combination in the practice of the present invention:

1. Perfluoroaliphatic anionic salts

Surfactants within this class are of the general formula described above wherein:

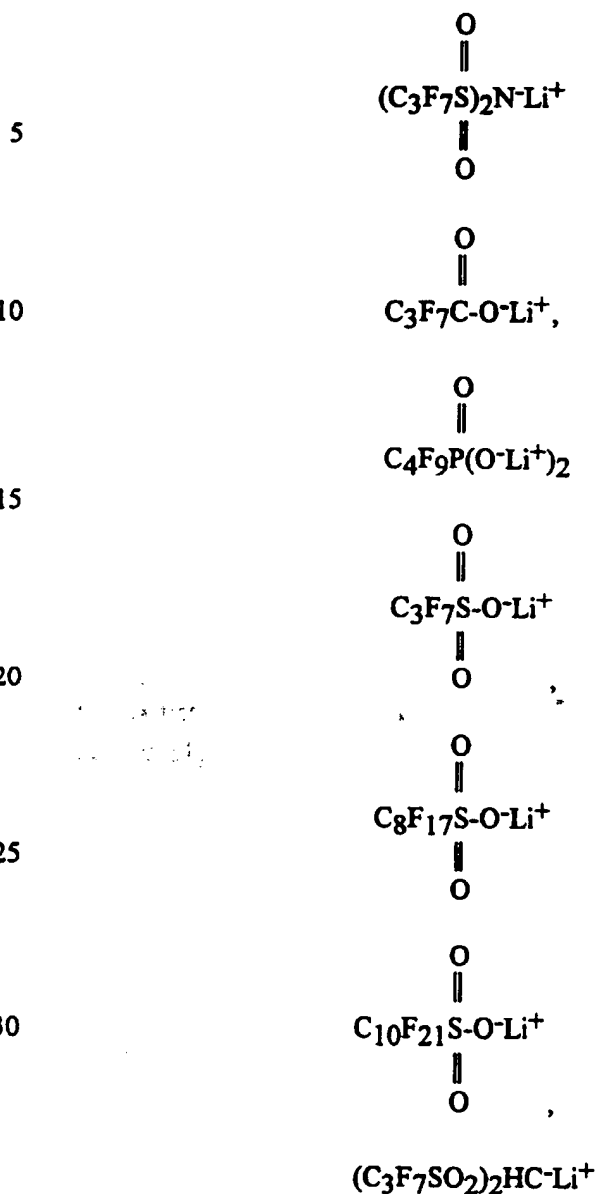
10



and wherein n is about 2 to 17, preferably about 3 to 12.

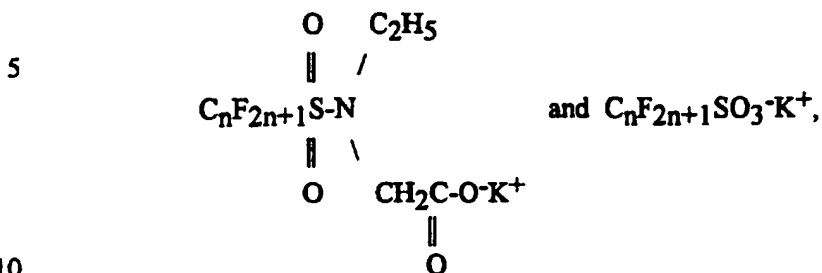
Preferred surfactants within this class include the lithium, sodium and potassium salts of anionic perfluoroaliphatic radical containing compounds. Some

15 particularly preferred lithium salts include the following:



Useful lithium salts are made following techniques disclosed in, for example, U.S. Pat. No. 2,732,398 (Brice et al.) and U.S. Pat. No. 2,809,990 (Brown), both incorporated herein by reference. Examples of commercially available lithium salts of anionic perfluoroaliphatic radical containing compounds include "Fluorad™ FC-122," "Fluorad™ FC-123" and "Fluorad™ FC-124 Fluorochemical Surfactants," from 3M Company, St. Paul, Minnesota.

Preferred potassium salts include:



wherein n is about 3 to 18, as well as mixtures of these salts.

Useful potassium salts are made by following techniques disclosed in, for example, U.S. Pat. No. 2,809,990 (Brown). Examples of commercially available potassium salts include "Fluorad™ FC-127," "Fluorad™ FC-129" and "Fluorad™ FC-95 Fluorochemical Surfactant," from 3M. A useful ammonium salt is commercially available as "Fluorad™ FC-120 Fluorochemical Surfactant" from 3M.

2. Perfluorinated radical substituted aliphatic anionic salts

Surfactants within this class are of the general formula described above,

wherein:

$$\text{R}^6 = (\text{C}_n\text{F}_{2n+1})_z \text{R}^7-$$

and wherein:

n is about 3 to 36, preferably 6 to 12;

R^7 is a branched or straight chain alkylene of about 2 to 36 carbon atoms, preferably 2 to 22 carbon atoms, or an aralkylene of about 7 to 36 carbon atoms, optionally independently substituted in available positions with oxygen, nitrogen or sulfur atoms, which R^7 group is selected such that R^6 comprises at least 7 carbon atoms; and

z is about 1 to 3, preferably 1 or 2.

Examples of commercially available salts of this class include "Zonyl FSA Fluorosurfactant" ($(F(CF_2CF_2)_{3-8}CH_2CH_2SCH_2CH_2CO_2^-Li^+)$ and "Zonyl FSE Fluorosurfactant" (a mixture of $F(CF_2CF_2)_{3-8}CH_2CH_2OP(O)(O-NH_4^+)_2$ and $[F(CF_2CF_2)_{3-8}CH_2CH_2O]_2P(O)(O-NH_4^+)$, from E.I. Du Pont de Nemours and Co.

3. Straight or branched chain aliphatic sulfates and sulfonates

Surfactants within this class are of the general formula described above, wherein:



and wherein:

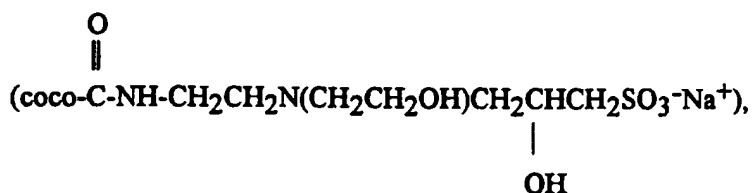
n is about 4 to 36,

R^7 is a branched or straight chain alkylene of about 2 to 36 carbon atoms, preferably 2 to 22 carbon atoms, or an aralkylene group of about 7 to 36 carbon atoms, optionally independently substituted in available positions with oxygen, nitrogen or sulfur atoms;

m is 0 or 1, and

L is SO_3^- or SO_4^- .

Examples of commercially available surfactants of this class include sodium dodecyl sulfate and sulfonates such as "Mackam CS"



where "coco" means a mixture of alkyl chain lengths derived from coconut oil fatty acid residues, "Mackham CBS-50 Amphoteric" (cocamido propyl hydroxyl sultaine) from The McIntyre Group Ltd., and "Hostastat HS-1" ($C_{10-18}H_{21-39}SO_3^-Na^+$), from Hoechst Celanese Corp.

4. Sulfates or Sulfonates of polyethoxylated derivatives of straight or branched chain aliphatic alcohols and carboxylic acids

5 Surfactants within this class are of the general formula described above, wherein:



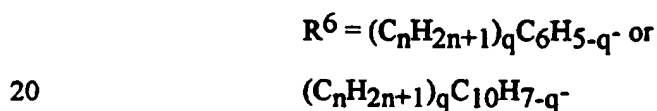
and wherein:

10 n is about 4-36,
p is 0 or 1 and
y is about 1-100, preferably 1-20; and wherein
L is SO_4^- or SO_3^- .

Examples of commercially available surfactants of this class include "Steol CA-460" ($C_{12}H_{25}O(CH_2CH_2O)_{12}SO_3^-Na^+$), from Stepan Co.

15 5. Alkylbenzene or alkylnaphthalene sulfonates and sulfates

Surfactants within this class are of the general formula described above, wherein:



and wherein:

n is about 4 to 36, preferably 8 to 22,
q is 1-3, preferably 1 or 2, and
L is SO_3^- or SO_4^- .

25 Examples of commercially available surfactants of this class include "Rhodocal DS-10" (sodium laurylbenzene sulfonate) from Rhone-Poulenc Co., "Polystep A-16" ($C_{12}H_{23}-C_6H_4-SO_3^-Na^+$) and "Polystep A-15," from Stepan Co., and "Poly-Tergent 2EP" from Olin Corp.

6. Ethoxylated and polyethoxylated alkyl and aralkyl alcohol carboxylates

Surfactants within this class are of the general formula described above, wherein:

$$5 \quad R^6 = (C_nH_{2n+1})_q(C_6H_5-q)_mO(CH_2CH_2O)_yCH_2-,$$

and wherein:

n is about 4 to 36, preferably 8 to 22,

m is 0 or 1, and

q is 1 or 2, preferably 1, and

10 y is about 1 to 100, preferably 1-20; and wherein

L is CO_2^-

Examples of commercially available surfactants of this class include

"Sandopan LS-24 Carboxylated Surfactant" ($C_{12}H_{25}O(CH_2CH_2O)_{12}CH_2COO^-$

Na^+), "Sandopan L8-HC Carboxylated Surfactant" and "Sandopan LA-8

15 Carboxylated Surfactant" ($C_{12}H_{25}O(CH_2CH_2O)_4CH_2COO^-Na^+$), from Sandoz Chemicals, Corp.

7. Glycinates

Surfactants within this class of the general formula described above, wherein:

20

$$R^6 = R^2-C(O)N(R^3)CH_2-,$$

wherein:

R^2 is a branched or straight chain alkyl of about 4 to 36 carbon atoms, preferably 8 to 22 carbon atoms, or an aralkyl group of about 7 to 36 carbon atoms, preferably 12 to 22 carbon atoms, which alkyl or aralkyl group is optionally independently substituted in available positions with oxygen, nitrogen or sulfur atoms; and

25

R^3 is hydrogen or an alkyl group of about 1 to 10 carbon atoms which may be optionally independently substituted in available positions by oxygen, nitrogen or sulfur atoms;

30

and wherein L is CO_2^- .

Examples of preferred surfactants within this class are alkyl sarcosinates and alkyl glycinate. Examples of commercially available surfactants of this class include "Hampshire C-30," ($\text{coco-C(O)N(CH}_3\text{)CH}_2\text{COO}^-\text{Na}^+$) from Hampshire Chemical Co., and "Mackam Amphoteric" (dihydroxyethyl tallow glycinate) from the McIntyre Group, Ltd.

8. Sulfosuccinates

Surfactants within this class are of the general formula described above, wherein:



and wherein:

R^2 is a branched or straight chain alkyl group of about 4 to 36 carbon atoms, preferably 8 to 22 carbon atoms, or an aralkyl group of about 7 to 36 carbon atoms, preferably 12 to 22 carbon atoms, which alkyl or aralkyl group may be independently substituted in available positions by oxygen, nitrogen and/or sulfur atoms; and

L is SO_3^- .

An example of a preferred surfactant of this class is dialkyl sulfosuccinate. Examples of commercially available surfactants of this class include "Aerosol™ OT Surface Active Agent" ($\text{C}_8\text{H}_{17}\text{OC(O)-CH(SO}_3^-\text{Na}^+)\text{CH}_2\text{C(O)O-C}_8\text{H}_{17}$) and "Aerosol™ TR Surface Active Agent" ($\text{C}_{13}\text{H}_{27}\text{-OC(O)-CH(SO}_3^-\text{Na}^+)\text{CH}_2\text{C(O)O-C}_{13}\text{H}_{27}$) from Cytec Industries.

9. Isethionate Derivatives

Surfactants within this class are of the general formula described above, wherein:



and wherein R^2 is a branched or straight chain alkyl group of about 4 to 36 carbon atoms, preferably 8 to 22 carbon atoms, or an aralkyl group of about 7 to 36 carbon atoms, preferably 12 to 22 carbon atoms, which alkyl or aralkyl

group is optionally independently substituted in available positions with oxygen, nitrogen or sulfur atoms; and

L is SO_3^-

5 Examples of commercially available surfactants of this class include "Igepon AC-78" (coconut acid ester of sodium isethionate), from GAF Corp., New York, New York.

10. N-acyltaurine Derivatives

Surfactants within this class are of the general formula described above wherein:

10 $\text{R}^6 = \text{R}^2\text{-C(O)N(R}^3\text{)CH}_2\text{CH}_2\text{-}$

and wherein R^2 is a branched or straight chain alkyl group of about 4 to 36 carbon atoms, preferably 8 to 22 carbon atoms, or an aralkyl group of about 7 to 36 carbon atoms, preferably 12 to 22 carbon atoms, which alkyl or aralkyl group is optionally independently substituted in available positions with oxygen,
15 nitrogen or sulfur atoms;

R^3 is hydrogen or an alkyl group of about 1 to 10 carbon atoms which may be optionally independently substituted in available positions by oxygen, nitrogen or sulfur atoms; and

L = SO_3^-

20 Examples of commercially available surfactants of this class include "Igepon T-77" (sodium N-methyl-N-oleyltaurate), from GAF Corp.

11. Amphoteric Alkyl Carboxylates

Surfactants within this class are of the general formula described above, wherein:

25
$$\begin{array}{c} \text{R}^8 \\ | \\ \text{L is } \text{N}^+\text{-(CH}_2\text{)}_x\text{COO}^-, \text{ wherein } \text{R}^8 \text{ is hydrogen, or an} \\ | \\ \text{R}^8 \end{array}$$

30

alkyl or alkylene carboxyl group of about 1 to 8 carbon atoms optionally substituted in available positions by nitrogen, oxygen or sulfur atoms, and x is 1 to 4; and

wherein R^6 is a branched or straight chain alkyl group of about 4 to 36 carbon atoms or an aralkyl group of about 7 to 36 carbon atoms which alkyl or aralkyl group is unsubstituted or independently substituted in available positions with oxygen, nitrogen or sulfur atoms.

Examples of preferred surfactants of this class are amphoteric propionates and alkyl and aryl betaines, optionally substituted with oxygen, nitrogen and/or sulfur atoms. Examples of commercially available surfactants of this class include "Tego Betain F-50" (coco-C(O)NH-CH₂CH₂CH₂ N⁺(CH₃)₂-CH₂COO⁻), from Goldschmidt Chemical Corp., "Mackam OB-30 Amphoteric" (C₁₈H₃₄N⁺(CH₃)₂CH₂COO⁻), "Mackam HV Amphoteric" (C₁₈H₃₄C(O)NHCH₂CH₂CH₂N⁺(CH₃)₂CH₂COO⁻) from the McIntyre Group, Ltd., "Miranol 2CIB" from Rhone-Poulenc, Co., and "Miratane AP-C" (coco₂-N⁺H-CH₂CH₂COO⁻) from Rhone-Poulenc Co.

12. Alkyl phosphate mono or di-esters

Surfactants within this class are of the general formula described above, wherein:

$R^6 = R^2O(CH_2CH_2O)_vCH_2CH_2-$, and wherein

R^2 is a branched or straight chain alkyl group of about 4 to 36 carbon atoms, preferably 8 to 22 carbon atoms, or an aralkyl group of about 7 to 36 carbon atoms, preferably 12 to 22 carbon atoms, optionally independently substituted in available positions with oxygen, nitrogen or sulfur atoms;

v is 0-100, preferably 0-20; and

L is PO₄⁻² or PO₄⁻.

Examples of commercially available surfactants of this class include "Rhodafac MC-470" (ethoxylated dodecyl alcohol phosphate ester, sodium salt) from Rhone-Poulenc, and "Sipostat 0012" (C₁₂H₂₅OP(O)(O-Na⁺)₂) and "Sipostat

0018" ($C_{18}H_{37}OP(O)(O^-Na^+)_2$) from Specialty Industrial Products, Inc.,
Spartanburg, South Carolina.

Applicants have discovered that the above-described anionic surfactants in combination with the surfactants of the present invention can be utilized in concentrations which are effective to provide adequate wetting and ensure a uniform coating while not significantly reducing the anti-fog or anti-reflective effects produced by the inorganic metal oxide. The anti-reflective property of the coating may be decreased by the surfactant by means similar to excess anionic silane, including reduction in the porosity and increase in the refractive index due to the refractive index of the surfactant itself. In general, an amount of surfactant is used which will ensure a uniform coating while not reducing either the anti-fog or anti-reflective properties. Surfactants of lower refractive indices may be tolerated at higher concentrations on a weight basis. For typical concentrations of metal oxide (e.g., about 1 to 5 percent by weight) most surfactants comprise less than about 0.1 percent by weight of the coating composition, preferably between about 0.003 and 0.05 percent by weight, in order to preserve the anti-reflective properties of the coating. It should be noted that with some surfactants a spotty coating is attained at concentrations in excess of what is needed to achieve the anti-fog property.

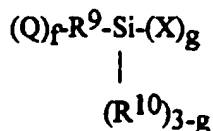
Where improved coating uniformity is desirable, it may be beneficial to add another wetting agent (in addition to the above-described surfactants), including those that do not impart durable anti-fog properties, in order to ensure uniform coating of the article from an aqueous or hydroalcoholic solution.

Examples of useful wetting agents include polyethoxylated alkyl alcohols (e.g. "Brij™ 30," and "Brij™ 35," commercially available from ICI Americas, Inc., and "Tergitol™ TMN-6 Specialty Surfactant," commercially available from Union Carbide Chemical and Plastics Co.), polyethoxylated alkylphenols (e.g., "Triton™ X-100" from Union Carbide Chemical and Plastics Co., "Iconol NP-70" from BASF Corp.) and polyethylene glycol/polypropylene glycol block copolymer (commercially available as "Tetronic™ 1502 Block Copolymer Surfactant," "Tetronic™ 908 Block Copolymer Surfactant" and "Pluronic F38 Block

Copolymer Surfactant," all from BASF, Corp.) Of course, any added wetting agent must be included at a level which will not destroy the anti-reflective or anti-fog properties of the coating. Generally the wetting agent is used in amounts of up to about 0.10 weight percent of the coating composition depending on the amount of inorganic metal oxide. Preferably the wetting agent is present in amounts less than 0.05, more preferably less than 0.03, weight percent of the coating composition. Alternatively, lower alcohols (C₁ to C₈) in the coating solution have proven useful in improving wetting.

The coating compositions of the present invention may also include a coupling agent capable of covalently bonding the surfactant to the metal oxide. Some coupling agents are capable of reacting with specific functional groups on the surface of the article to be coated. Consequently, the coupling agent may be capable of promoting adhesion of the coating composition to the substrate. The coupling agent has at least two reactive functionalities. One reactive functionality is capable of covalently bonding to the metal oxide and the second is capable of covalently bonding to the surfactant. For example, reactive functionalities such as amino, hydroxyl, mercaptan, acrylate and methacrylate groups present on one compound (the surfactant, coupling agent, or the metal oxide) can react with complementary reactive functionalities, such as oxirane, chloro-, bromo-, iodo-, alkyl, aziridine, anhydride, acrylate, methacrylate, or isocyanato groups, present on the other compound (coupling agent or surfactant). More than one coupling agent may be used. For example, two types of coupling agents which are capable of covalently bonding to each other may be employed where one coupling agent is capable of covalently bonding to the metal oxide and the other is capable of covalently bonding to the surfactant.

Useful silane coupling agents include those with the following formula:



wherein:

R^9 is a substituted or unsubstituted divalent hydrocarbon bridging group of about 1 to 20 carbon atoms, optionally including in the backbone 1 to 5 moieties selected from the group consisting of -O-, -C(O)-, -S-, -SO₂- and -NR"- groups, and optionally substituted on the backbone by -OH, -SH, or -NR"-₂, wherein R" is hydrogen, acetyl, or a hydrocarbon group of 1 to 6 carbon atoms;

X is -OR¹² where R¹² is an alkyl, aryl, heteroaryl, or aralkyl group of 1 to 8 carbon atoms, preferably methyl or ethyl; or -N=C(R¹³)₂, wherein R¹³ is independently an alkyl, aryl or aralkyl group of 1 to 8 carbon atoms;

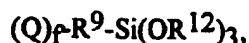
R¹⁰ is independently an alkyl, aryl, aralkyl or alkoxy group of 1 to 8 carbon atoms optionally substituted in available positions by oxygen, nitrogen and/or sulfur atoms;

f is 0, 1, or 2;

g is 2 or 3; and

Q is a reactive functional group capable of reacting with complementary functionalities on the surface of the substrate or the surfactant. Examples of Q include amino; hydroxyl; mercaptan; oxirane; chloro-, iodo-, and bromo-alkyl; aziridine; cyclic carboxylic anhydride; acrylate; methacrylate; acrylamide, azide, and isocyanato groups. It should be understood that when present in the coating compositions of the invention (particularly with base stabilized sols) the coupling agents will hydrolyze, in which case one or more of the "X" or "OR²" groups will be converted to a silanol or silanolate.

Preferred silanes have the structure:



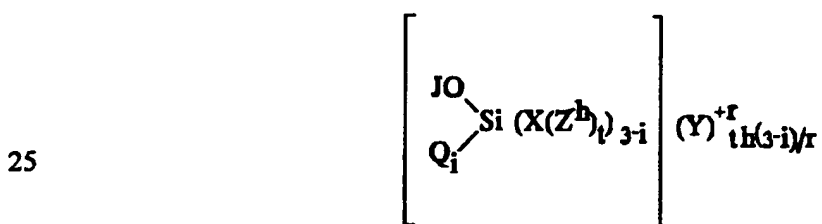
wherein Q is preferably a primary or secondary epoxy or amino group and R⁹ and R¹² are as described above.

Additional information on ambifunctional silane coupling agents may be found in European Patent Application No. 0,372,756 A2. Alternatively the coupling agent can be a titanate or zirconate compound, such as "Tyzor Titanate," commercially available from Du Pont.

The amount of coupling agent included in the coating composition should be limited in order to prevent destruction of the anti-reflective or anti-fog properties of the coating. The optimal amount of coupling agent is easily determined experimentally and is a function of the coupling agent's identity, molecular weight and refractive index. The coupling agent(s), when present, are typically added to the composition at levels of 0.1 to 20 percent by weight of the metal oxide concentration, and more preferably about 1 to 10 percent by weight of the metal oxide. Tetraalkoxy coupling agents, such as tetraethylorthosilicate (TEOS) and oligomeric forms such as alkyl silicates (e.g. poly(diethoxy siloxane)), may also be useful to improve binding between metal oxide particles.

Additional materials capable of bonding with the metal oxide and improving the durability of the anti-fog coatings of this invention include anionic silane agents. Preferred anionic silanes (described below) which are capable of themselves providing anti-fog properties to substrates or articles coated therewith. Such preferred anionic silanes are described in PCT WO96/18918, filed November 30, 1995. The term anionic silane as used herein describes organofunctional silicon containing compounds capable of hydrolyzing to organosilanol with subsequent condensation to organofunctional siloxane oligomers.

The preferred anionic silane compounds useful in the solutions and compositions of the present invention have the following general structure:



wherein:

Q is selected from the group consisting of hydroxyl, alkyl groups containing from 1 to about 4 carbon atoms, and alkoxy groups containing from 1 to about 4 carbon atoms;

J is selected from cations derived from the group consisting of hydrogen, alkali metals and organic cations of strong bases having an average molecular weight of less than about 150 and a pKa of greater than about 11;

X is an organic linking group;

5 Z is selected from the group consisting of $-\text{OSO}_2\text{O}^-$, $-\text{SO}_2\text{O}^-$, $-\text{CO}_2^-$, $(-\text{O})_2\text{P}(\text{O})\text{O}^-$, $-\text{P}(\text{O})(\text{O}^-)_2$, $-\text{OP}(\text{O})(\text{O}^-)_2$, $-\text{P}(\text{O}^-)_2$ and $-\text{OP}(\text{O}^-)_2$;

Y is selected from cations derived from the group consisting of hydrogen, alkali metals, alkali earth metals, organic cations of weak bases having an average molecular weight of less than about 200 and a pKa of about 8 to 11 (e.g.,
 10 $\text{HN}^+(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_3$ and $\text{H}_2\text{N}^+(\text{CH}_2\text{CH}_2\text{OH})_2$), organic cations of strong bases having an average molecular weight of less than about 150 and a pKa of greater than about 11, substituted and unsubstituted guanidines, and quaternary ammonium cations (e.g. $\text{N}^+(\text{CH}_3)_4$, $\text{N}^+(\text{CH}_2\text{CH}_3)_4$ and N^+H_4); provided that J is hydrogen when Y is selected from cations derived from hydrogen, alkaline earth
 15 metals and said weak organic bases;

r is equal to the valence of Y and is 1 to 3;

h is 1 or 2;

i is 1 or 2; and

t is 1 to 3.

20

Preferably Z is sulfonate (SO_2O^-) or phosphonate ($-\text{P}(\text{O})(\text{O}^-)_2$) or carboxylate (CO_2^-), more preferably sulfonate and phosphonate, and the preferred anionic silane is an organosilanol, such as the sulfonato-organosilanols disclosed in U.S. Patent 4,235,638 to Beck, incorporated herein by reference. Alternatively, the
 25 anionic silane may be one of those disclosed in U.S. Patent Nos. 3,816,184; 4,344,860; or 4,370,255. The organic linking group X, is preferably selected from alkylene groups, cycloalkylene groups, hydroxy-substituted alkylene groups, hydroxy-substituted mono-oxa alkylene groups, divalent hydrocarbon groups having mono-oxa backbone substitution, divalent hydrocarbon groups having
 30 mono-thia backbone substitution, divalent hydrocarbon groups having monooxa-

thia backbone substitution, divalent hydrocarbon groups having dioxo-thia backbone substitution, arylene groups, arylalkylene groups, alkylarylene groups, and alkylarylene groups, all of which groups may be substituted by N, O and/or S atoms and all of which X groups comprise from about 1 to 20 carbon atoms, preferably from about 1 to 6 carbon atoms. Most preferably X is selected from alkylene groups, hydroxy-substituted alkylene groups and hydroxy-substituted mono-oxa alkylene groups.

In order to ensure optimum hydrophilicity and maximize the durability of the coating, the preferred anionic organosilanol preferably has a relatively high percentage of oxygen on a weight percentage basis. Preferably, the weight percent oxygen is at least about 30%, more preferably at least about 40%, and most preferably in the range of about 45 to 55%. In general, the weight percent silicon in these compounds is no greater than about 15%. Each of these percentages is based on the weight of the compound in the water-free acid form. Aqueous or hydroalcoholic solutions of the organosilanol-sulfonic acids (i.e. Z is SO_3^- and Y is hydrogen) are acidic generally having a pH of less than about 5 while the organosilanol-sulfonate salts are basic and generally have a pH of greater than about 9.0. In order to prevent destabilization of the preferred base stabilized metal oxide sols the organo-silanol-sulfonate salt form is preferred.

The anionic organosilanol may be applied as part of the metal oxide and/or surfactant containing coating composition or may be applied as an "overcoat", i.e. can be applied as a separate coating solution applied over a previously deposited metal oxide and/or surfactant containing coating. Preferably, the anionic organosilanol is added directly to the metal oxide sol and surfactant-containing coating composition to simplify the coating process and to minimize any risk of scratching the metal oxide layer.

The preferred anionic organosilanols are most conveniently applied from an aqueous or hydroalcoholic solution and therefore may be partially or completely hydrolyzed to the silanol/silanolate form and may include oligomeric siloxane forms of the anionic organosilanol. The level of organosilanol must be kept relatively low with respect to the metal oxide concentration in order to prevent reduction in the

anti-reflective property. The anti-reflective property may be decreased by one or both of two means. Firstly, if too much organosilanol is added the porosity (void volume) of the coating decreases, thereby increasing the refractive index of the coating beyond that desired for maximum transmission of light. Secondly the refractive index of the silane itself might influence the refractive index of the coating if the amount of silane becomes excessive. In general, the highest level of anionic silane which will not adversely affect the anti-reflective property or coating quality is preferred. The anionic silanes are preferably added to the coating composition at a concentration of about 5 to 50% by weight of the metal oxide. More preferably the anionic silanes are added to the coating composition at a concentration of about 10 to 30% by weight of the metal oxide, in order to preserve the anti-reflective properties of the coating.

The coating composition may optionally contain a polymeric binder to improve scratch resistance and/or adhesion of the coating composition to the substrate. Useful polymeric binders are preferably water soluble or water swellable and include polymers comprised of ethenically unsaturated monomer(s), such as polyvinyl alcohol, polyvinylpyrrolidone, polyvinyl acetate, polyacrylates and methacrylates and polyurethanes; polyesters; natural polymers such as starch, gelatin, gums, celluloses, dextran, proteins and the like; and derivatives (ionic and non-ionic) and copolymers based on any of the polymers listed above. Furthermore, polymers comprising alkoxysilane functionalities may also be useful. The coating composition can contain up to about 5 weight percent of the polymeric binder based on the weight of the inorganic metal oxide. Useful amounts of polymeric binder are generally in the range of about 0.05 to 5 weight percent by weight to improve scratch resistance and coating adhesion.

It is also possible to apply a primer coating to improve adhesion of the coating to the substrate. A particularly preferred primer material is polyvinylidene chloride (PVDC).

Articles

Substrates to which the coating compositions of the invention can be applied are preferably transparent or translucent to visible light. Preferred substrates are

made of polyester (e.g., polyethylene terephthalate, polybutyleneterephthalate), polycarbonate, allyldiglycolcarbonate, polyacrylates, such as polymethylmethacrylate, polystyrene, polysulfone, polyethersulfone, cellulose acetate butyrate, glass and the like, including blends and laminates thereof.

5 Typically the substrate is in the form of a film, sheet, panel or pane of material and is part of an article such as ophthalmic lenses, architectural glazings, decorative glass frames, motor vehicle windows and windshields, and protective eye wear, such as surgical masks and face shields. The coatings may if desired, cover only a portion of the article, e.g., only the section immediately adjacent the eyes in a face
10 shield may be coated. The substrate may be flat, curved or shaped. The article to be coated may be produced by blowing, casting, extrusion, or injection molding.

Articles such as disposable surgical face masks and face shields which are coated with the anti-reflective, anti-fog compositions of this invention are preferably stored in single use packages which reduce environmental exposure and
15 contamination which can result in decreased anti-fog properties. Reusable articles are preferably used in combination with a package that protects or completely seals the product from environmental exposure when not in use. The material used to form the packages should be comprised of a non-contaminating material. It has been found that certain materials can result in partial or total elimination of the anti-
20 fog properties. While not being bound by any theory, it is currently believed that materials which contain plasticizers, catalysts, and other low molecular weight materials which can volatilize on aging are sorbed into the coating and result in a decrease in the anti-fog property. For example, packaging materials such as polyurethane foams, plasticized polyvinylchloride and low density polyethylene have
25 been found to significantly reduce the anti-fog properties of the articles of the present invention, especially when in direct contact with the coating. Currently preferred packaging materials include paper and bleached paper products, such as bleached white bond paper, cardboard, and clay-coated solid white bleached sulfate boxboard, and/or films or laminates made from polyester, high density polyethylene,
30 or polystyrene.

Process

The compositions of the present invention are preferably coated on the article using conventional techniques, such as bar, roll, curtain, rotogravure, spray, or dip coating techniques. The preferred methods include bar and roll coating or air knife coating to adjust thickness. In order to ensure uniform coating and wetting of the film, it is convenient to oxidize the substrate surface prior to coating using corona discharge or flame treatment methods. These methods may also improve adhesion of the coating to the substrate. Other methods capable of increasing the surface energy of the article include the use of primers such as thin coatings of polyvinylidene chloride (PVDC). The coatings of the present invention are preferably applied in uniform average thicknesses varying by less than about 200Å, and more preferably by less than 100Å, in order to avoid visible color variations in the coating. The optimal average dry coating thickness is dependent upon the particular coating composition, but in general the average thickness of the coating is between 500 and 2500Å, preferably 750 to 2000Å, and more preferably 1000 to 1500Å, as measured using an ellipsometer such as a Gaertner Scientific Corp. Model No. L115C. Above and below this range, the anti-reflective properties of the coating may be significantly diminished. It should be noted, however, that while the average coating thickness is preferably uniform, the actual coating thickness can vary considerably from one particular point on the coating to another. This variation in thickness, when correlated over a visibly distinct region, may actually be beneficial by contributing to the broad band anti-reflective properties of the coating.

The coatings of the present invention are preferably coated on both sides of the substrate. Alternatively, the coatings of the present invention may be coated on one side of the substrate. The opposite side of the substrate may be:

- a. uncoated,
- b. coated with a conventional surfactant or polymeric anti-fogging composition such as that disclosed in US Patent Nos. 2,803,552; 3,075,228; 3,819,522; 4,467,073; or 4,944,294, or
- c. coated with an anti-reflective composition, such as that disclosed in US Patent No. 4,816,333, or the multiple layered coating described by J.D. Masso in

"Evaluation of Scratch Resistant and Anti-reflective Coatings for Plastic Lenses," (supra). Preferably, the coating surface should face the direction of higher humidity, e.g., on a face shield the side having the anti-fog coating should face the wearer.

5 Once coated, the article is typically dried at temperatures of between 20° and 150°C in a recirculating oven. The temperature may be increased further to speed the drying process, but care must be exercised to avoid degradation of the substrate. The preferred coating compositions are preferably dried at between 50° and 120°C and most preferably between 100° and 110°C. After the coating is
10 applied to the substrate and dried, it comprises preferably from about 85 to 99.7 percent by weight (more preferably from about 88 to 95 percent by weight) metal oxide, about 0.25 to 5 percent by weight (more preferably from about 0.2 to 2 percent by weight) surfactant, up to about 25 percent by weight (more preferably from about 5 to 15 percent by weight) coupling agent and up to about 5 percent by
15 weight (preferably up to about 2 percent by weight) wetting agent.

 When the coating compositions of the invention are applied to substrates to provide anti-reflection properties, glare is reduced by increasing the light transmission of the coated substrate. The percent transmission is dependent upon the angle of incidence and the wavelength of light and is determined using ASTM
20 test method D1003-92, entitled "Haze and Luminous Transmittance of Transparent Plastics". Preferably, the coated substrates display an increase in percent transmission of at least 3 percent, more preferably greater than 5 percent, and most preferably greater than 8 percent when compared with an uncoated substrate, measured using 550 nm light (e.g., the wavelength at which the human eye displays
25 peak photo-optic response). When the desired usage involves significant "off-axis" (i.e., non-normal) viewing or unwanted reflections, gains in visibility may be greater especially where the reflections approach or exceed in brightness the object in view.

 The coating compositions of the invention, as discussed hereinabove, provide anti-fog as well as anti-reflective properties to surfaces coated therewith.
30 The anti-fog property is demonstrated by the tendency of the coatings to resist the formation of water droplets which tend to significantly reduce the clarity or

transparency of the coated substrate. Water vapor from, for example, human breathing, tends to condense upon the coated substrate in the form of a thin uniform water film, rather than as water droplets. Such a uniform film does not significantly reduce the transparency of the substrate. For example, using the "Wetting Test" described in the Examples, when a 3 microliter drop of water is placed on the surface of a substrate coated with the coating composition of the invention, the drop spreads to an initial diameter of at least 6mm, preferably at least 7mm, and most preferably at least 8mm due to the hydrophilic nature of the anti-fog/anti-reflective coating.

The coating compositions of the present invention are durable and shelf stable, e.g., they do not deteriorate significantly when allowed to be exposed at 23°C and 50% relative humidity for up to sixteen weeks. Preferred coatings when exposed at 30°C and 60% relative humidity in a recirculated environmental chamber (the circulation rate = 1.67 vol./min.) for at least fourteen days, and, more preferably, at least twenty-one days, and most preferably twenty-eight days, and tested according to the "Wetting Test" described in the examples, have a 3 microliter drop diameter of at least 4mm, and more preferably at least 5mm.

Examples

The surfactants present in the anti-fog/anti-reflective compositions of Examples 1 through 12 and Comparative Examples A through F are described in Table 1.

TABLE I

Ex. No.	Surfactant Class	Chemical Description	Trade Name	Source	Address
1, 3	Alkyl or aralkyl polyglucoside	alkyl (C _{12.5}) polyglucosides	Glucopon™ 625CS Surfactant	Henkel Corp./Emery Group	Amber, PA
2	Alkyl or aralkyl polyglycerol ester	p-isononyl phenoxy polyglycerol	Surfactant 10G	Olin Corp.	Stamford, CT
4	Alkyl or aralkyl pyrrolidone	alkyl(C ₈)-pyrrolidone C ₁₂ H ₂₃ NO	Surfadone™ LP-100 Specialty Surfactant	ISP Technologies	Wayne, NJ
5	Alkyl or aralkyl glyceryl ester	glycerol monolaurate	Luaricidin™ Surfactant	Luaricidin Inc.	East Lansing, MI
6	Alkyl or aralkyl glyceryl ester	glycerol monostearate	Cerasynt GMS	ISP Van Dyk Inc.	Belleville, NJ
7	Alkyl or aralkyl sorbitam esters	sorbitan monooleate	Span 80	ICI Americas Inc.	Wilmington, DE
8	Alkyl or aralkyl polyglycerol ester	6-glycerol-2-oleate	Caprol 6G2O	Karishamns USA Corp.	Columbus, OH
9	Alkyl or aralkyl polyglycerol ester	6-glycerol-2-stearate	Caprol 6G2S	Karishamns USA Corp.	Columbus, OH
10	Alkyl or aralkyl polyglucoside	alkyl polyglucoside	Montanov 68	Seppic Inc.	Fairfield, NJ
11	Alkyl or aralkyl diethanolamide	lauric diethanolamide	Chemstat LD-100	Chemax	Greenville, SC
12	Alkyl or aralkyl diethanolamide	stearyl diethanolamide	Lipamide S	Lipo Chemical	Paterson, NJ
Comp A	Polyethoxylated alkyl phenol	nonionic - polyethoxylated octyl phenols	Triton™ X-100 Specialty Surfactant	Union Carbide Chemical & Plastics Co., Industrial Chemicals Division	Danbury, CT
Comp B	Polyethoxylated alkyl alcohol	nonionic - polyoxyethylene (23)lauryl ether	Brij™ 35 Nonionic Surfactant	ICI Americas Inc.	Wilmington, DE
Comp C	Block copolymers of polyethylene oxide and polypropylene oxide	nonionic - block copolymer of polyethylene oxide and polypropylene oxide, ethylene diamine started (PEG/PPG/PEG block copolymer)	Tetronic™ 1502 Block Copolymer Surfactant	BASF Corp., Performance Chemicals	Parsippany, NJ
Comp D	Amine oxide	nonionic/ cationic - lauryl dimethylamine oxid	Rhodamox™ LO Specialty Surfactant	Rhone-Poulenc, Surfactant & Specialty Divisio	Cranberry, NJ
Comp E	Polyethoxylated alkyl alcohol	nonionic - polyethoxylated trimethyl- nonanol	Tergitol™ TMN-6 Specialty Surfactant	Union Carbide Chemical & Plastics Co.	Danbury, CT
Comp F		ammonium xylene sulfonate		Reutgers-Neese Chemical Co.	State College, P

Example 1 and Comparative Examples A-C

The anti-fog/anti-reflective compositions of Example 1 and anti-reflective compositions of Comparative Examples A-C were prepared by adding the surfactants described in Table 1 in the amounts given in Table 2 to a 1.75 weight percent dispersion of silica sol, commercially available as "Remasol SP-30 Sodium Stabilized Silica Sol (30 percent solution)" from Remet Corp., Chadwicks, NY, in deionized water. The compositions were coated on both sides of a 0.18 mm (7 mil) thick flame treated polyethylene terephthalate (PET) film using a roll coater with an air knife to adjust thickness to a violet to slightly blue hue (approximately 1,000 to 1,200Å). The coated film was immediately passed into a forced air drier at a temperature of 77°C. The dwell time in the oven was less than 2 minutes. The films were evaluated for fog resistance the day the coated film samples were made ("initial fog") and again after aging 12 days in ambient conditions of approximately 23°C and 50 percent relative humidity. Fogging was evaluated by breathing directly on the film with the film held approximately 2.5 cm from the mouth. Initial fog was determined subjectively as "excellent," "good," "okay," and "poor" depending upon the relative ability to see through the film after breathing upon it. The following numerical ratings were used for the 12 day evaluation: "1" means the coated film fogs like the uncoated film; "2" means the coated film fogs after 1-2 consecutive breaths; "3" means the coated film had a light fog after 3 consecutive breaths; "4" means the coated film had a very light fog after 4 consecutive direct breaths; and "5" means the coated film resisted fogging after 5 consecutive direct breaths. The results of the initial fogging and 12 day fogging are reported in Table 2.

TABLE 2

Ex. No.	Surfactant Concentration (weight %)	Initial Fog	Fog After 12 days Aging
Comp. A	0.150	good	2
Comp. B	0.014	good	2
Comp. C	0.015	poor	2
1	0.014	good	5

Discussion of Results: The films which were coated with compositions containing the surfactants in Comparative Example A and B were resistant to fogging initially

but were easily fogged after aging for only 12 days. The film which was coated with a composition containing the surfactant used in Comparative Example C was easily fogged initially and after aging. The film which was coated with a composition containing a surfactant in accordance with the present invention had good resistance to fogging initially and after aging for 12 days. All of the coated films, when visually compared with uncoated film by holding the films up to a beige surface under incident light, were significantly more transparent and anti-reflective than the uncoated film.

Example 2

A 2.5 weight percent dispersion of the silica sol "Remasol SP-30 Sodium Stabilized Silica Sol (30 percent solution)" was prepared in deionized water. A silane coupling agent, glycidoxypopyl trimethoxy-silane (GPS), commercially available as "A-187" from Union Carbide Chemical & Plastics Company, was added to the sol at a concentration of 0.25 weight percent in solution. The anti-fog/anti-reflective composition of Example 2 was made by adding the surfactant described in Table 1 to a concentration of 0.015 weight percent. The composition was coated on both sides of 0.18 mm (7 mil) thick PET film using a number 6 Meyer bar. The first side was coated and immediately dried at 100 C for 1-2 minutes. Next the second side was coated and also dried at 100 C for 1-2 minutes. The coated film was aged in a 49°C recirculated oven and was evaluated for fogging at regular time intervals using the Fog Test described below. The coating composition provided an anti-reflective surface when evaluated using the test described in Example 1.

Fog Test: Individual film samples were held over a steam source for approximately 5 seconds. The steam source was a container of boiling deionized water which was equipped with a funnel or other device that allowed the steam to exit approximately 10-13 cm above the liquid level through an opening which is approximately 1.3 cm in diameter. The steam temperature was approximately 55°C. The film sample was held approximately 5-8 cm above the steam exit. The results were determined subjectively as "excellent," "good," "trace," "fair" and "poor" depending on the relative ability to see through the film during the test. The coated film of Example 2 had only a trace of fog after testing following 16 days of aging.

Examples 3-4 and Comparative Examples D-F

The anti-fog/anti-reflective compositions of Examples 3 and 4 and the anti-reflective compositions of Comparative Examples D-F were prepared as follows. A master batch of colloidal silica was made using "Remasol SP-30 Sodium Stabilized Silica Sol" (30 percent solution), GPS, commercially available as "G6720 GPS" from Huls, Piscataway, NJ, and deionized water in the following amounts:

	<u>Material</u>	<u>Amount (g)</u>
10	Deionized Water	142,600
	Colloidal silica	8,840
	GPS	265

The materials were added in the order listed with a minimum of 5 minutes of mixing between additions. The mixture was allowed to stir overnight. To prepare each coating composition, the surfactant listed in Table 1, in the amount and concentration described in Table 3, was added to 18,900 gram aliquots of the master batch solution. The compositions were coated onto a 30.5 cm wide, 0.18 cm (7 mil) corona discharge treated PET film using a roll coater and air knife as described in Example 1. The air knife was operated at a pressure of approximately 5-13 cm of water. The setting varied with each composition in order to attain the desired thickness of coating, which had a violet to slightly blue hue. The coated films were immediately passed into a forced air drier at a temperature of 77°C. The dwell time in the oven was less than 2 minutes. The second side was coated in a similar manner. All of the coating compositions provided an anti-reflective surface, as determined using the test for anti-reflection described in Example 1. The coating quality was evaluated visually and the following rating scale was used: "excellent" means virtually no coating defects, a uniform finish; "very good" and "good" indicate only minor coating inconsistencies; "poor" means many coating inconsistencies. The results are reported qualitatively in Table 3.

TABLE 3

Ex. No.	Amount of 4% surfactant solution (g)	Surfactant Concentration (weight %)	Coating Quality
3	71.0	0.015	very good
4	37.7	0.008	very good
Comp. D	37.8	0.008	good
Comp. E	56.7	0.012	good
Comp. F	66.2	0.014	good

The coated films were aged using the Aging Test described below.

Aging Test: Multiple coated film samples were cut, 5 cm x 15 cm. Great care was taken to keep the coated film samples from becoming contaminated. Personnel wore cotton gloves and samples were not placed in packaging materials which could result in surface contamination. A magazine was made using styrofoam core/paper board, with razor slits approximately 1.3 cm deep and 1.3 cm apart cut into one edge of the board. The coated film samples were placed in the magazine so that adjacent samples were not touching and so that substantially the entire surface area of the sample was exposed to the environment. The sample loaded magazines were placed in a totally recirculated and recycled oven. The oven conditions were: 1) a recirculation rate of 1.67 volumes/minute, 2) a temperature of 30°C, and 3) a relative humidity of 60 percent. It was possible that in some samples an increase in fogging was a result of surface contamination due to the air quality inside the oven. Therefore, relative differences are more important than the actual values. Film samples were removed at regular time intervals of 7, 14, 28, 56 and 84 days and evaluated using the Wetting Test described below. The "initial" sample was evaluated after standing at room temperature for 24 to 48 hours after coating.

Wetting Test: This test measures the degree of wetting of the various coatings. Surfaces which are hydrophilic and, thus, anti-fog will exhibit average drop diameters in excess of 4 mm. Each film sample was conditioned at 23°C and 50 percent relative humidity for a minimum of 8 hours before and during testing. Care was taken to ensure that the film samples were not contaminated and that exposure to the environment did not result in decreased wetting. The film samples

were placed on a clean flat horizontal surface with the side to be tested up. A 3 microliter drop of deionized and distilled water containing 0.07% by weight "Wool Fast Brilliant Red R.L. Dye," commercially available from Pylam, Garden City, NY, from an accurate syringe was gently placed on the surface by holding the syringe vertically and just touching the drop to the surface so that the drop did not fall and impact the surface. The drop was allowed to spread to its maximum extent and completely dry. The diameter of the drop was determined by placing the film over a paper with premeasured circles of varying diameters. The average drop diameter was recorded. The dye did not interact with the surfactant system being tested, as verified by comparing the results with and without the dye. The results of the Wetting Test are reported in Table 4.

TABLE 4

Ex. No.	Wetting Value after Aging					
	Initial (mm)	Day 7 (mm)	Day 14 (mm)	Day 28 (mm)	Day 56 (mm)	Day 84 (mm)
3	8.82	6.83	5.83	4.83	3.84	.1
4	8.55	6.56	5.60	4.38	3.93	3.84
Comp. D	8.73	4.29	3.93	3.84	3.84	3.56
Comp. E	8.55	5.56	4.38	3.97	3.84	3.56
Comp. F	8.87	5.11	4.65	3.93	3.93	3.56

¹ Sample was not tested at this time interval

Discussion of results: Uncoated PET film had a wetting value of 2.75 mm for comparison. Actual breathing tests such as those described in Example 1 indicated that once the wetting values fall below about 4.1 mm the fogging was unacceptable for use in a surgical mask application. The surfactants of the present invention produced coated films with acceptable wetting values (indicating no tendency to fog) beyond day 28 in this accelerated aging test. The coated films of Comparative Examples E and F lost their anti-fog properties between day 14 and day 28, and the coated film of Comparative Example D by day 14.

Aging in Sealed Environment

In order to better understand the aging properties of the various surfactants and whether environmental contamination of the films decreases their anti-fog property, coated films from Examples 3, 4 and Comparative Example D were

conditioned in a 25°C/50 % relative humidity environment for 24 hours and were placed in two sets of sealed jars. Separate jars were used for coated films containing different surfactants. Jars in Set 1 (Dry) contained only the coated films, while jars in Set 2 (Wet) contained the coated films and a small vial of deionized water. The water in the vial did not contact the films directly, but served as a source of humidity. The jars were placed in a 40°C oven and films were periodically withdrawn and tested for Wetting as described above. The results are reported in Table 5 for dry aging (Set 1) and Table 6 for wet aging (Set 2). The coated films containing the surfactants of the present invention performed extremely well as durable anti-fogging agents when maintained in a sealed chamber. The fogging characteristics did not significantly decrease even after 56 days. The wetting of Comparative Example D fell rapidly even in a sealed container. While not being bound to any theory, the results indicated that loss of anti-fog properties may be due to environmental surface contamination of the coated film. Loss of anti-fog properties in the comparative example appeared to be due to other causes since the anti-fog property decreased very rapidly even in a sealed container.

TABLE 5

Ex. No.	Set 1 "Dry" Wetting Value after Aging					
	Initial (mm)	Day 7 (mm)	Day 14 (mm)	Day 28 (mm)	Day 56 (mm)	Day 84 (mm)
3	8.82	7.28	7.46	8.91	9.64	8.73
4	8.55	6.56	6.19	8.91	8.82	7.73
Comp. D	8.73	4.65	4.47	4.83	3.75	4.02

TABLE 6

Example Number	Set 2 "Wet" Wetting Value after Aging				
	Initial (mm)	Day 7 (mm)	Day 14 (mm)	Day 28 (mm)	Day 56 (mm)
3	8.82	8.28	7.55	8.10	7.64
4	8.55	7.82	7.55	8.37	7.10
Comp. D	8.73	4.38	4.06	3.93	4.11

Examples 5-12

The anti-fog/anti-reflective compositions of Examples 5a-c, 6a-c, 7a-c, 8a-c, 9a-c, 10a-c, 11a-c and 12a-c were prepared by adding the surfactants described in Table 1, in the amounts given in Table 7, to 50 g of a 1.75 weight percent dispersion of "Remasol SP-30 Sodium Stabilized Silica Sol (30 percent solution)" in

deionized water. The surfactants of Examples 5, 6, and 10 were dissolved at 2 weight percent in isopropyl alcohol. Those of Examples 8, 9, 11, and 12 were dissolved at 2 weight percent in deionized water. The compositions were coated on one side of a corona discharge treated 0.18 mm (7 mil) thick PET film using a number 6 wire wound Meyer bar. The films were immediately placed in a 100 C forced air drying oven. Next the second side of the film was coated using the same method. The coating solutions were coated at room temperature, except that the coating of Example 10 was coated at 75°C. The coating quality was determined visually and the following rating scale was used: "excellent" means virtually no coating defects, a uniform finish; "very good" means very few minor coating inconsistencies; "good" means only minor coating inconsistencies; "spotty" means some coating inconsistencies; and "very spotty" means many coating inconsistencies. The results for the coating quality are reported in Table 7.

All of the coating compositions provided an anti-reflective surface, as determined using the test for anti-reflection described in Example 1. The coated films were aged using the Aging Test described in Examples 3 and 4 except that the entire magazine of film samples was placed inside a paperboard box to minimize air borne contamination. After aging for 13, 21, 28 and 35 days the films were evaluated using the Wetting Test also described in Examples 3 and 4. The results of the Wetting Test are also reported in Table 7.

TABLE 7

Ex. No.	Amount of 2% surfactant solution added (g)	Coating Quality	Wetting Value after Aging				
			Initial (mm)	Day 13 (mm)	Day 21 (mm)	Day 28 (mm)	Day 35 (mm)
5 a	0.20	good	8.0	7.7	7.9	5.5	4.3
5 b	0.35	good	8.3	7.6	8.2	6.7	5.4
5 c	0.50	good	8.5	7.6	8.6	7.4	4.7
6 a	0.20	very good	8.1	6.9	7.9	6.1	4.6
6 b	0.35	very good	7.5	7.6	7.7	7.0	4.6
6 c	0.50	very good	8.1	7.0	7.4	5.7	4.3
7 a	0.20	spotty	8.1	8.1	8.4	8.5	7.5
7 b	0.35	spotty	8.1	7.7	8.3	8.4	8.2
7 c	0.50	very good	7.9	7.8	8.4	8.4	9.0
8 a	0.20	spotty	8.3	8.2	8.4	7.0	6.6
8 b	0.35	spotty	8.1	7.7	8.5	6.7	5.5
8 c	0.50	very spotty	7.8	7.8	8.6	7.6	6.4
9 a	0.20	excellent	8.9	8.6	8.6	8.5	7.6
9 b	0.35	excellent	8.6	7.4	8.6	8.2	7.7
9 c	0.50	very good	8.5	8.5	8.4	7.1	4.9
10 a	0.20	very good	8.6	8.4	8.5	7.9	7.1
10 b	0.35	very good	8.6	8.2	8.4	7.3	5.9
10 c	0.50	very good	8.4	7.9	8.0	6.5	5.3
11 a	0.20	excellent	8.9	8.3	8.8	7.6	1
11 b	0.35	excellent	9.3	8.8	8.9	8.4	1
11 c	0.50	excellent	9.5	8.9	9.1	8.3	1
12 a	0.20	good	8.1	7.9	7.7	5.4	1
12 b	0.35	very good	7.7	7.7	8.1	5.1	1
12 c	0.50	very good	7.8	7.7	7.8	4.7	1

1 "-" indicates film was not evaluated at this time interval.

Discussion of results: The results indicate that the coating quality and anti-fog properties (as indicated by the wetting values) were affected by surfactant concentration. For each composition the anti-fog property was quite durable as demonstrated by Wetting Values in excess of 4.1 mm even after 35 days of accelerated aging. The coatings of Examples 7, 9 and 11 were very durable as indicated by their high Wetting Values.

Claims

1. A coating composition which imparts anti-reflection and anti-fogging properties to a substrate having a surface coated therewith, the coating composition comprising:

- (a) inorganic metal oxide particles; and
- (b) a surfactant comprised of at least one hydrophobic group and at least one hydrophilic group, wherein

(1) the hydrophilic group is selected from the group consisting of

(i) pyrrolidone, and

(ii) a polyhydroxyl group comprising at least two

hydroxyl groups, wherein at least two of the hydroxyl groups are separated by no more than 5 atoms, and the number of said hydroxyl groups is greater than or equal to the total number of hydrophobic groups present within the surfactant molecule, and

(2) wherein the hydrophobic group is a hydrocarbon chain

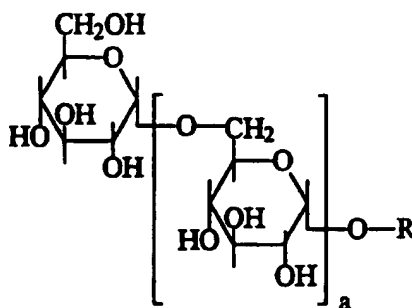
comprising at least 4 carbon atoms or a perfluorinated radical comprising at least 3 carbon atoms,

and wherein the coating composition when coated on at least one side of a light transmissive substrate:

1) exhibits a drop diameter of at least 4 mm when tested in accordance with the Wetting Test described herein; and

2) provides said substrate with a percent transmission at 550 nm which is at least 3 percent greater than that of the uncoated substrate.

2. The coating composition of claim 1 wherein the surfactant has the general formula:



wherein

R is an alkyl or aralkyl group having about 4 to 36 carbon atoms, an aralkyl group having about 7 to 36 carbon atoms, or a perfluorinated alkyl group having about 3 to 12 carbon atoms, and

a is between 0 and 20.

3. The coating composition of claim 1 wherein the surfactant has the general formula:



wherein

R is an alkyl group having about 4 to 36 carbon atoms, an aralkyl group having about 7 to 36 carbon atoms, or a perfluorinated alkyl group having about 3 to 12 carbon atoms.

4. The coating composition of claim 1 wherein the surfactant has the general formula:



wherein

Y is OH or an alkyl group having about 8 to 36 carbon atoms, or an aralkyl group having about 7 to 36 carbon atoms, or a perfluorinated alkyl group having about 3 to 12 carbon atoms, and

n is between about 2 and 20.

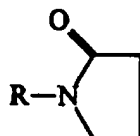
5. The coating composition of claim 1 wherein the surfactant has the general formula:



wherein

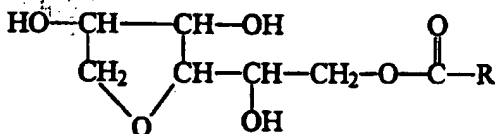
R is an alkyl group having about 4 to 36 carbon atoms, an aralkyl group having about 7 to 36 carbon atoms, or a perfluorinated alkyl group having about 3 to 12 carbon atoms.

- 5 6. The coating composition of claim 1 wherein the surfactant has the general formula:



- 10 wherein R is an alkyl group having about 4 to 36 carbon atoms, an aralkyl group having about 7 to 36 carbon atoms, or a perfluorinated alkyl group having about 3 to 12 carbon atoms.

7. The coating composition of claim 1 wherein the surfactant has the general formula:



- 15 where R is an alkyl group having about 4 to 36 carbon atoms, an aralkyl group having about 7 to 36 carbon atoms, or a perfluorinated alkyl group having about 3 to 12 carbon atoms.

8. The coating composition of claim 1 wherein the inorganic metal oxide is selected from the group consisting of aluminum oxide, tin oxide, titanium oxide, antimony oxide, silica, zirconium oxide and mixtures thereof.

- 20 9. The coating composition of claim 1 further comprising:
a second surfactant comprised of at least one hydrophobic group and at least one hydrophilic anionic group, wherein:

- 25 (i) the hydrophilic anionic group comprises an anion selected from the group consisting of $-\text{OSO}_2\text{O}^-$, $-\text{SO}_2\text{O}^-$, $-\text{CO}_2^-$, $(-\text{O})_2\text{P}(\text{O})\text{O}^-$, $-\text{OP}(\text{O})(\text{O}^-)_2$, $-\text{P}(\text{O})(\text{O}^-)_2$, $-\text{P}(\text{O}^-)_2$, $-\text{OP}(\text{O}^-)_2$, $(-\text{SO}_2)_2\text{N}^-$, $-\text{SO}_2\text{N}(\text{R}'')^-$,

- 5 $(-\text{SO}_2)_2\text{C}-\text{H}$, and $-\text{N}^+(\text{R}'')_2(\text{CH}_2)_x\text{L}'$, wherein R'' is hydrogen, an alkyl group which is unsubstituted or substituted with atoms independently selected from the group consisting of oxygen, nitrogen and sulfur, or an alkylene carboxyl group, which alkyl or alkylene carboxyl group comprises about 1 to 10 carbon atoms; x is 1 to 4; and L' is selected from the group consisting of $-\text{OSO}_2\text{O}^-$, $-\text{SO}_2\text{O}^-$, $(-\text{O})_2\text{P}(\text{O})\text{O}^-$, $-\text{OP}(\text{O})(\text{O}^-)_2$, $-\text{P}(\text{O})(\text{O}^-)_2$ and $-\text{CO}_2^-$; and wherein each anionic group is associated with or covalently bound to at least one cation, which cation is selected from the group consisting of H^+ , Na^+ , K^+ , Li^+ , Ca^{+2} , Mg^{+2} , Sr^{+2} , Al^{+3} , and $\text{R}'''\text{A}^+$, wherein R''' is R^4 or R^5
- 10 wherein R^4 is hydrogen or an alkyl or cycloalkyl group of about 1 to 10 carbon atoms, and R^5 is covalently bonded to the surfactant molecule and is an alkyl bridging group of 1 to 10 carbon atoms, and A^+ is N^+R^4_3 , a guanidinium ion optionally substituted with oxygen, nitrogen or sulfur atoms, or N^+B wherein B comprises 3 to 7 atoms selected from the group consisting of carbon, nitrogen, sulfur and oxygen atoms which complete the nitrogen containing heterocyclic ring; and wherein any R^4 or R^5 group may be unsubstituted or substituted with atoms independently selected from the group consisting of oxygen, nitrogen or sulfur; the cation selected such that the net charge of the surfactant molecule is neutral; and
- 15 (ii) wherein the hydrophobic group comprises a hydrocarbon chain comprising at least 4 carbon atoms, or a perfluorinated radical comprising at least 3 carbon atoms.
- 20

25 10. The coating composition of claim 1 further comprising a silane coupling agent capable of covalently bonding the metal oxide to the surfactant or substrate.

11. An article comprising a substrate having a surface and a layer of a coating composition according to claim 1 on at least one surface of the substrate which coating composition has been dried.

30 12. An article according to claim 11 wherein the surface is plastic or glass.

13. An article according to claim 11 wherein the substrate is transparent or translucent to visible light incident thereon.

14. An article according to claim 11 wherein the layer of the coating composition provides a continuous network of inorganic metal oxide particles.

5 15. An eye shield comprising a substrate which is transparent or translucent to visible light coated with

(a) a porous inorganic metal oxide network of uniform average thickness which provides anti-reflection properties to the substrate; and

(b) a surfactant comprised of at least one hydrophobic group and at least one hydrophilic group, wherein

(1) the hydrophilic group is selected from the group consisting of

(i) pyrrolidone, and

(ii) a polyhydroxyl group comprising at least two

hydroxyl groups, wherein at least two of the hydroxyl groups are separated by no more than 5 atoms, and the number of said hydroxyl groups is greater than or equal to the total number of hydrophobic groups present within the surfactant molecule, and

(2) wherein the hydrophobic group is a hydrocarbon chain comprising at least 4 carbon atoms or a perfluorinated radical comprising at least 3 carbon atoms;

which coated substrate:

1) exhibits a drop diameter of at least 4 mm when tested in accordance with the Wetting Test described herein; and

2) provides said substrate with a percent transmission at 550 nm which is at least 3 percent greater than that of the uncoated substrate.

16. A surgical mask comprising a face mask and an eye shield according to claim 15.

17. A method of imparting anti-reflection and anti-fogging properties to a substrate, the method comprising the steps of:

(a) providing a substrate;

(b) preparing a coating composition comprising:

- (1) a porous inorganic metal oxide; and
- (2) a surfactant comprised of at least one hydrophobic group and at least one hydrophilic group, wherein

- (a) the hydrophilic group is selected from the group consisting of
 - (i) pyrrolidone, and
 - (ii) a polyhydroxyl group comprising at least two hydroxyl groups, wherein at least two of the hydroxyl groups are separated by no more than 5 atoms, and the number of said hydroxyl groups is greater than or equal to the total number of hydrophobic groups present within the surfactant molecule, and

- (b) wherein the hydrophobic group is a hydrocarbon chain comprising at least 4 carbon atoms or a perfluorinated radical comprising at least 3 carbon atoms;

- (c) applying the coating composition to at least one side of the substrate; and

- (d) drying the coating composition.

18. The method of claim 17 wherein the substrate is transmissive to visible light and the metal oxide and surfactant are present in the coating composition in amounts sufficient to provide the coated light transmissive substrate

- 1) with a drop diameter of at least about 4 mm when tested in accordance with the Wetting Test described herein; and
- 2) with a percent transmission at 550 nm which is at least 3 percent greater than that of the uncoated substrate.

19. A method of imparting anti-reflection and anti-fogging properties to a substrate, the method comprising the steps of:

- (a) providing a substrate;
- (b) preparing a first coating composition comprising inorganic metal oxide particles;

(c) preparing a second coating composition comprising a surfactant comprised of at least one hydrophobic group and at least one hydrophilic group, wherein

(1) the hydrophilic group is selected from the group consisting of

(i) pyrrolidone, and

(ii) a polyhydroxyl group comprising at least two hydroxyl groups, wherein at least two of the hydroxyl groups are separated by no more than 5 atoms, and the number of said hydroxyl groups is greater than or equal to the total number of hydrophobic groups present within the surfactant molecule, and

(2) wherein the hydrophobic group is a hydrocarbon chain comprising at least 4 carbon atoms or a perfluorinated radical comprising at least 3 carbon atoms,

(d) applying either the first or second coating composition to at least one side of the substrate;

(e) allowing the coating applied in step (d) to dry;

(f) applying the coating composition not applied in step (d) to at least one side of the substrate;

(g) allowing the coating applied in step (f) to dry.

20. The method of claim 19 wherein the substrate is light transmissive and the amount of metal oxide and surfactant applied to the substrate is sufficient to provide the coated substrate with

1) a drop diameter of at least about 4 mm when tested in accordance with the Wetting Test described herein; and

2) a percent transmission at 550 nm which is at least 3 percent greater than that of the uncoated substrate.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 96/18986

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09D1/00 C09D5/00 C09K3/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D C08J C09K C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 171 (C-0706), 3 April 1990 & JP 02 022342 A (SEKISUI CHEM CO LTD), 25 January 1990, see abstract	1
A	--- PATENT ABSTRACTS OF JAPAN vol. 015, no. 286 (M-1138), 19 July 1991 & JP 03 101926 A (SEKISUI CHEM CO LTD), 26 April 1991, see abstract --- -/--	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* "A" document member of the same patent family

Date of the actual completion of the international search

8 April 1997

Date of mailing of the international search report

29. 04. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+ 31-70) 340-3016

Authorized officer

Niaounakis, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/18986

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9414 Derwent Publications Ltd., London, GB; Class A23, AN 94-111895 XP002029100 & JP 06 041 335 A (SKC KK) , 15 February 1994 cited in the application see abstract ---	1
A	US 3 826 127 A (MOLINA O) 30 July 1974 see claim 1 see column 2, line 52 - line 65 ---	1
A	EP 0 460 382 A (HELLA KG HUECK & CO) 11 December 1991 see claims 1,4 ---	1
A	US 4 310 330 A (FUNAKI MASAOKI ET. AL) 12 January 1982 see claim 1 see column 4, line 28 - column 5, line 12 ---	1
P,A	WO 96 18691 A (MINNESOTA MINING & MFG) 20 June 1996 see claims 1,9,13 -----	1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/18986

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3826127 A	30-07-74	US 3939101 A	17-02-76
EP 0460382 A	11-12-91	DE 4017341 A	05-12-91
		DE 59106967 D	11-01-96
		ES 2082028 T	16-03-96
US 4310330 A	12-01-82	JP 1425480 C	15-02-88
		JP 56005358 A	20-01-81
		JP 62025792 B	04-06-87
		AU 543517 A	26-04-85
		AU 5954180 A	08-01-81
		DE 3022980 A	29-01-81
		FR 2459260 A	09-01-81
WO 9618691 A	20-06-96	AU 4372396 A	03-07-96